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(54) METHOD FOR PRODUCING MOLYBDENUM-BISMUTH-IRON CONTAINING COMPOSITE OXIDE FLUID BED CATALYST

(57) One object of the present invention is to provide a method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst, which is useful for an ammonoxidation and which produces a target ammonoxidation product at high yield and an excellent reproducibility. In order to achieve this object, the present invention provides a method for producing a molybde-

num-bismuth-iron containing composite oxide fluid bed catalyst which is used for ammonoxidation of organic compounds, comprising the step in that a slurry, which contains the raw materials containing specific elements, is subjected to a concentration treatment at 50-120°C.

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Description**TECHNICAL FIELD**

5 [0001] The present invention relates to a method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst. Specifically, the present invention relates to a method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst, which is used for an ammonoxidation of many kinds of organic compounds.

10 BACKGROUND ART

[0002] Many catalysts, which are suitably used in methods for producing an ammonoxidation product by ammonoxidation of olefins, are disclosed in numerous documents. Examined Japanese Patent Application, Second Publication No. Sho 38-17967 discloses an oxide catalyst containing molybdenum, bismuth, and iron. Examined Japanese Patent Application, Second Publication No. Sho 38-19111 discloses an oxide catalyst containing iron and antimony. After these oxide catalysts were improved diligently, many improved oxide catalysts were suggested. For example, Examined Japanese Patent Application, Second Publication No. Sho 51-33888, Unexamined Japanese Patent Application, First Publication No. Sho 55-56839, Examined Japanese Patent Application, Second Publication No. Sho 58-2232, Examined Japanese Patent Application, Second Publication No. Sho 61-26419, Unexamined Japanese Patent Application, First Publication No. Hei 07-47272, Unexamined Japanese Patent Application, First Publication No. Hei 10-43595, Unexamined Japanese Patent Application, First Publication No. Hei 04-118051, and the like disclose solutions for improving an oxide catalyst by adding molybdenum, bismuth, iron, and other components and by adding iron, antimony, and other components.

[0003] In addition, in order to improve a yield of a target product, methods for producing an oxide catalyst have been examined. For example, Unexamined Japanese Patent Application, First Publication No. Hei 06-9530 discloses examples showing a method in which a slurry is heated at 90°C for three hours. Japanese Patent 2,640,356 and Unexamined Japanese Patent Application, First Publication No. Hei 01-265068 disclose a method in which a pH of a slurry is adjusted to 5 or less and it is heated to 50-120°C. Japanese Patent 2,747,920, Unexamined Japanese Patent Application, First Publication No. Hei 02-251250, Unexamined Japanese Patent Application, First Publication No. 2000-5603, Unexamined Japanese Patent Application, First Publication No. 2000-344724, Unexamined Japanese Patent Application, First Publication No. 2000-37631, and Unexamined Japanese Patent Application, First Publication No. 2000-42414 disclose a method in which a pH of a slurry is adjusted to 6 or more and it is heated to 50-120°C.

[0004] As disclosed in Examined Japanese Patent Application, Second Publication No. Sho 58-8895, in chemical products, which are produced by an oxidation or an ammonoxidation of olefins, marvelous economical effects can be obtained by increasing only 1% of a yield thereof. Due to this, research to improve the catalysts is constantly being performed.

[0005] Conventional catalysts gradually improve a yield of target ammonoxidation products. However, conventional catalysts do not achieve sufficient yield. In addition, it has been an objective to produce a catalyst having a high activity at high yield and an excellent reproducibility, as one of serious problems to be solved.

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DISCLOSURE OF INVENTION

[0006] As a result of conducting diligent research, the present inventors have demonstrated that a catalyst which yields an objective ammonoxidation product, having a high activity at high yield and an excellent reproducibility, can be produced by concentrating a slurry containing specified metal elements under specified conditions.

[0007] In other words, the present invention relates to a method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst which is a method for producing a composite oxide catalyst containing components (1) molybdenum, (2) bismuth, (3) iron, (4) nickel, (5) at least one element selected from lithium, sodium, potassium, rubidium, cesium and thallium, and (6) silica, as essential components, wherein a slurry containing at least components (1), (2), (3), and (6) is subjected to a concentration treatment in a range of 50-120°C, so that the concentration difference of the slurry between before and after the concentration treatment is in a range of 2-15% by mass.

MODES FOR CARRYING OUT THE INVENTION

55 [0008] The present invention is explained in detailed below.

[0009] In order to produce the fluid bed catalyst in the present invention, in a method for producing a composite oxide catalyst containing components (1) molybdenum, (2) bismuth, (3) iron, (4) nickel, (5) at least one element selected from lithium, sodium, potassium, rubidium, cesium and thallium, and (6) silica, as essential components, a slurry con-

taining at least components (1), (2), (3), and (6) is subjected to a concentration treatment in a range of 50-120°C, so that the concentration difference of the slurry between before and after the concentration treatment is in a range of 2-15% by mass. If one of these requirements is not satisfied, the objects of the present invention cannot be achieved.

5 [0010] The concentration treatment denotes a step in which a slurry concentration after a concentration treatment is increased by evaporating moisture contained in the slurry. In the concentration treatment, an evaporation rate of moisture is preferably adjusted. In order to adjust the evaporation rate, a reflux apparatus may be used. In addition, the concentration treatment may be also carried out while the evaporation amount of moisture is adjusted by adding water.

10 [0011] The slurry, which is subjected to the concentration treatment, must contain at least components (1), (2), (3), and (6). The catalyst, which produces a high ammonoxidation product yield, is produced with an excellent reproducibility by concentrating the slurry containing components (1), (2), (3), and (6). Moreover, it is not necessary for the slurry to contain the required total amount of these components in the concentration treatment; a part of amount of the component may be added to the slurry after the concentration treatment.

15 [0012] The reasons for improving the yield of the ammonoxidation products by the concentration treatment are not clear. However, it is believed that by the concentration treatment, a compound or a precursor which is suitable for improving the catalyst activity is formed. Otherwise, it is also believed that precipitates in the slurry become finer in good progress and the slurry is stabilized. Due to this, it is believed that a catalyst having superior properties is produced with a good reproducibility.

20 [0013] A slurry temperature in the concentration treatment is preferably in a range of 50-120°C, and more preferably in a range of 90-120°C. When the slurry temperature is less than 50°C, there are cases in which sufficient effects cannot be obtained. When it exceeds 120°C, the effects can be obtained, but the system used for the concentration treatment must be pressurized, and this is not economical. During the concentration treatment, the pressure may be reduced, normal, or increased. However, the concentration treatment is preferably carried out under reduced pressure or normal pressure. In particular, normal pressure is more preferable economically.

25 [0014] The duration of the concentration treatment is not restricted, in particular. In general, the concentration treatment is carried out for 30 minutes or longer, and more preferably it is carried out for 1-10 hours. The concentration treatment, of which the duration exceeds 24 hours, is not preferably in production efficiency.

30 [0015] The concentration difference of the slurry between before and after the concentration treatment is preferably in a range of 2-15% by mass, and more preferably in a range of 3-14% by mass. The slurry concentration denotes the ratio of mass of stabilized oxides, which are final products when the component elements contained in the slurry are changed into stabilized oxides, with respect to the total mass of the slurry. When the concentration difference of the slurry before and after the concentration treatment is less than 2% by mass, sufficient effects cannot be obtained. In contrast, when it exceeds 15% by mass, the viscosity of the slurry increases and there is a possibility that a problem may be generated in a spray-drying step after the concentration treatment. Due to this, the slurry concentration after the concentration treatment is preferably in a range of 15-35% by mass, and more preferably in a range of 16-30% by mass.

35 [0016] Conditions of the slurry, which is subjected to the concentration treatment, is not restricted. However, the slurry, of which the pH is adjusted in a range of 1-4, is preferable. In the slurry having pH of 1-4, silica sol, which is used as a raw material of silica, is in a metastable state. Almost all of silica sol is in a liquid phase. In conventional methods for producing the catalyst, there are cases in which conditions of a spray-drying step which is necessary to produce a catalyst having sufficient particle strength to practical use, are restricted. However, according to the present invention, when the slurry having a pH of 1-4 is used, by conducting the concentration treatment, not only the yield of ammonoxidation products is improved, but also the particle strength is improved. Therefore, in the present invention, the restriction to conditions of a spray-drying step decreases, and productivity of catalyst is improved.

40 [0017] The reasons for improving the particle strength by the concentration treatment are not clear. However, it is believed that by the concentration treatment, a crystal growth of silica or a cross-linking formation in silica is expedited.

45 [0018] When a pH of the slurry is relatively low, a method disclosed in Japanese Patent 2,640,356 can be adopted. In contrast, when a pH of the slurry is relatively high, a method disclosed in Japanese Patent 2,747,920 can be adopted. In addition, in order to prevent the slurry from gelling, a chelating agent, such as ethylene diamine tetra-acetic acid, lactic acid, citric acid, tartaric acid, gluconic acid, and the like, can be added in the slurry as disclosed in Japanese Patent 2,747,920. When a small amount of the chelating agent is added to the slurry having a relatively low pH, such as 1-3, the effects for preventing the gellation of slurry are sometimes obtained.

50 [0019] The composition of the catalyst, which is produced by the present invention, is not restricted, as long as it contains components (1) molybdenum, (2) bismuth, (3) iron, (4) nickel, (5) at least one element selected from lithium, sodium, potassium, rubidium, cesium and thallium, and (6) silica, as essential components. However, the method of the present invention is preferably used to produce the catalyst represented by the following formula.

Mo10 Bla Feb Nic (FeSbd)e Ff Gg Hh Mm Xx Yy Oi(SiO₂)j

5 [0020] In the formula, Mo, Bi, Fe, Ni, and (FeSbd) denote molybdenum, bismuth, iron, nickel, and iron antimonate. F denotes at least one element selected from yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, aluminum, and gallium. G denotes at least one element selected from magnesium, calcium, strontium, barium, chromium, manganese, cobalt, copper, zinc, and cadmium. H denotes at least one element selected from titanium, zirconium, vanadium, niobium, tantalum, tungsten, germanium, tin, lead, and antimony. M denotes at least one element selected from ruthenium, rhodium, palladium, rhenium, osmium, iridium, platinum, and silver. X denotes at least one element selected from boron, phosphorus, and tellurium. Y denotes at least one element selected from lithium, sodium, potassium, rubidium, cesium, and thallium. O denotes oxygen. SiO₂ denotes silica. Symbols a, b, c, d, e, f, g, h, m, x, y, i, and j denote atomic ratio. When the atomic ratio of Mo is 10, a is in a range of 0.2-1.5, and preferably in a range of 0.3-1.2; b is in a range of 0.7-15, and preferably in a range of 0.8-13; c is in a range of 3-12, and preferably in a range of 4-10; d is in a range of 0.8-2, and preferably in a range of 0.9-1.5; e is in a range of 0-20; f is in a range of 0.1-1.5, and preferably in a range of 0.2-1.4; g is in a range of 0-3; h is in a range of 0-5; m is in a range of 0-1.0; x is in a range of 0-3; y is in a range of 0.05-1.5, and preferably in a range of 0.08-1.2; i is a number of oxygen element in metal oxides, which are formed by combining these elements; and j is in a range of 20-200, and preferably in a range of 30-150.

10 [0021] Raw materials of these elements contained in the catalyst are not restricted. For example, the raw material of the molybdenum component contains molybdenum oxides such as molybdenum trioxide; molybdcic acid and molybdcic acid salt such as ammonium paramolybdate, and ammonium methmolybdate; heteropoly acid containing molybdenum, such as phosphomolybdcic acid, and silicomolybdcic acid and heteropoly acid salt thereof.

15 [0022] The raw material of the bismuth component includes, for example, salts of bismuth, such as bismuth nitrate, bismuth carbonate, bismuth sulfate, bismuth acetate; bismuth trioxide; metal bismuth, and the like. These raw materials of bismuth component can be used as a solid as it is, an aqueous solution, a nitrate solution, or a slurry containing a bismuth compound, which is produced from the aqueous solution or the nitrate solution. However, bismuth nitrates, a solution containing bismuth nitrates, and a slurry produced from the solution are preferably used as the raw material of the bismuth component.

20 [0023] The raw material of the iron component includes, for example, ferrous oxide, ferric oxide, triron tetroxide, ferrous nitrate, ferric nitrate, iron sulfate, iron chloride, organic acid salt of iron, iron hydroxide, and the like, in addition to a solution which is produced by solving metal iron in hot nitric acid.

25 [0024] The raw material of the nickel component includes, for example, nickel nitrate, nickel hydroxide, nickel oxide, and the like.

30 [0025] The raw material of the silica component includes, for example, silica sol, humid silica, and the like. However, silica sol is conveniently used. In general, the raw material of the other elements includes, oxides, and nitrates, carbonates, organic acid salts, hydroxides, and mixture thereof, which are changed into oxides by calcination.

35 [0026] When iron antimonate is contained in the catalyst, it is preferable to prepare iron antimonate and to mix with molybdenum and other components, and thereby a slurry is produced. Iron antimonate is represented by chemical formula FeSbO₄, as disclosed in Unexamined Japanese Patent Application, First Publication Nos. Hei 04-118051 and Hei 10-231125. The presence of iron antimonate can be confirmed by an X-ray diffraction analysis. Many methods for producing the iron antimonate have been suggested. For example, the method may be selected from the methods disclosed in Unexamined Japanese Patent Application, First Publication Nos. Hei 04-118051 and Hei 10-231125. Iron antimonate may contain a small amount of elements other than antimony and iron. The presence of the iron antimonate improves the selectivity of ammonoxidation products and properties of the fluid bed catalyst.

40 [0027] The slurry produced by the concentration treatment in the present invention is changed to the objective fluid bed catalyst by spray drying and calcining.

45 [0028] A spray dryer used for spray drying the slurry produced by these processes includes, for example, ordinal rotary-disc type spray dryers, and ordinal nozzle type spray dryers, and the like. The catalyst having an objective particle diameter, which is suitable for a fluid bed catalyst, is produced by adjusting the conditions of the spray drying.

50 [0029] After drying, the dried product is calcined at 200-500°C, and this is further calcined at 500-700°C for 0.1-20 hours. The calcining is preferably carried out in an oxygen containing gas atmosphere. The calcining is conveniently carried out in air, but this may be carried out in a mixed gas containing oxygen, nitrogen, carbon dioxide gas, water vapor, and the like. Box furnaces, tunnel calciners, rotation calciners, fluidized bed calciners, and the like may be used for the calcining. Among these, fluidized bed calciners are preferably used.

55 [0030] The particle diameter of the fluid bed catalyst produced by these processes is in a range of 5-200 µm, and preferably in a range of 10-150 µm.

[0031] The catalyst produced by the present invention may be used for an ammonoxidation of organic compounds. The organic compound used for an ammonoxidation using the catalyst produced by the present invention includes, for

example, olefins, alcohols, ethers, aromatic compounds, heteroaromatic compounds, and the like. Specifically, the organic compound includes, for example, propylene, isobutene, methanol, ethanol, tert-butanol, methyl tert-butylether, toluene, xylene, picoline, quinaldine, and the like. In particular, if the catalyst produced by the present invention is used for an ammonoxidation of propylene, isobutene, methanol, and tert-butanol, preferable results are obtained.

5 [0031] In general, the ammonoxidation is carried out under conditions in which the molar ratio between the raw organic compound/ ammonia/ air is 1/0.9-3/8-12, and reaction temperature is in a range of 370-500°C, and reaction pressure is in a range of normal pressure to 500 kPa. Apparent contact time is in a range of 0.1-20 seconds. Air is conveniently used as an oxygen source, but air, which is diluted with water vapor, nitrogen, carbon dioxide gas, saturated hydrocarbons, and the like, is also used. In addition, oxygen enriched air is also used.

10 [0032] When the fluid bed catalyst having a stable catalytic structure, which is produced by the present invention, is successively used for the ammonoxidation, the molybdenum component is dispersed, and a yield of ammonoxidation products decreases. The reaction temperature of the ammonoxidation using the fluid bed catalyst exceeds 400°C. It is impossible to prevent the dispersion of molybdenum component during the ammonoxidation reaction. As a method for maintaining the properties of a catalyst for a long time, a method in which a molybdenum component is added to the 15 catalyst during reaction has been suggested in Examined Japanese Patent Application, Second Publication No. Sho 58-57422, DE 3,311,521-C2, and WO 97/33863.

20 [0033] In the present invention, in order to maintain high yield of ammonoxidation products for a long time, it is preferable to add a molybdenum component during an ammonoxidation reaction. The molybdenum component, which is added to the catalyst during reaction, includes, for example, metal molybdenum, molybdenum trioxide, molybdate acid, ammonium dimolybdate, ammonium paramolybdate, ammonium octamolybdate, ammonium dodecamolybdate, phosphomolybdate acid, and the like. These molybdenum components can be used as gas or liquid. However, in practice, the molybdenum component in a solid state is used. In addition, these molybdenum components may be supported with inactivated materials or the catalyst. In particular, a method, in which the molybdenum component is enriched in the catalyst, is effective. Since this method has excellent utilization efficiency, and prevent generation of the problems due to a deposition of molybdenum oxide in the reaction system, this method is preferable. A method for producing molybdenum enriched catalyst disclosed in Unexamined Japanese Patent Application, First Publication No. Hei 11-33400 and the like, can be adopted.

25 [0034] The molybdenum component is added successively or intermittently into a reactor. The timing of addition and the amount added may be determined depending on a reaction progress. However, the amount added of the molybdenum component at a time is preferably in a range of 0.05-2% by mass with respect to 100% by mass of the catalyst, which has already added. When an excess amount of the molybdenum component is added at a time, the molybdenum component is dispersed out of the reaction system, and this is wasted. In addition, an excess amount of the molybdenum component is deposited in the reactor, and this may lead to problems in operation of the reactor.

30 [0035] Below, the present invention will be explained with Examples and Comparative Examples.

Catalyst Activity Test

40 [0036] A catalyst activity test was carried out utilizing an ammonoxidation of propylene as follows. The results of the activity test are shown in Tables 1-3 and 1-4 below.

[0037] The catalyst was filled in a fluid bed reactor comprising a catalyst fluidized portion having an inner diameter of 25 mm and a height of 400 mm. After that, a mixture gas containing propylene, ammonia, air, and water vapor (mixing molar ratio of propylene/ ammonia/ air/ water vapor is 1/ 1.2/ 9.5/ 0.5) was introduced into the fluid bed reactor such that a gas linear velocity was 4.5 cm/sec. The reaction pressure was adjusted to 200 kPa.

45 [0038] During the reaction, a catalyst in which the molybdenum component was enriched, was added such that 0.1-0.2% by mass of molybdenum contained in the added catalyst with respect to 100% by mass of the filled catalyst was added at intervals of 100-500 hours.

50 Contact time (sec.) = Catalyst volume (ml) based on apparent bulk density / Gas flow rate (ml/ sec.) converted by reaction conditions

55 Yield (%) of acrylonitrile = Molar number of produced acrylonitrile / Molar number of supplied propylene X 100

Catalyst Strength Test

[0039] Strength of the catalyst particles produced in Examples and Comparative Examples was measured according to a method disclosed in Unexamined Japanese Patent Application, First Publication No. Hei 9-70542 as follows, and the strength of the catalyst particles are shown in Tables 1-3 and 1-4 below as a compressive strength (N/particle).

5 Use device: Shimazu MCTM-200 (marketed by Shimazu Corporation)

Pressure element: upper pressure element, which is made of diamond and which has a flat end surface having a diameter of 500 μm , and lower pressure plate, which is made of SUS

10 Pressure ratio: 7.06×10^{-3} N/sec

10 Sample: catalyst having a particle diameter of 45-50 μm

[0040] The catalyst having a particle diameter of 45-50 μm was prepared by sieving using Micro-Mesh@ Precision Sieves marketed by Buckbee-Mears St. Paul Company. Thirty particles, which were randomly selected from particles having a diameter of 45-50 μm , were used as samples. The average compressive strength of the thirty particles was the compressive strength of the sample.

15 Example 1

[0041] A fluid bed catalyst of which the composition is represented by $\text{Mo10 Bi0.4 Fe1.2 Ni6.0 Ce0.3 Cr0.8 P0.1 B0.1 K0.2 O1 (SiO}_2\text{)35}$ (I, which is an atomic ratio of oxygen, is determined depending on a valence of other elements, and therefore, the atomic ratio of oxygen will be omitted below) was produced by the following processes.

[0042] 409.4 g of ammonium paramolybdate was dissolved in 300 g of pure water. After that, 2.7 g of 85%-phosphoric acid and 0.5 g of boric anhydride were further added. A solution, in which 45.0 g of bismuth nitrate, 4.7 g of potassium nitrate, 404.7 g of nickel nitrate, 74.2 g of chromium nitrate, 30.2 g of cerium nitrate, and 25.0 g of citric acid were added to 270 g of 3.3%-nitric acid, was mixed with the prepared solution. After that, 2438.6 g of 20%-silica sol was also added. A solution, in which 112.4 g of iron nitrate and 25.0 g of citric acid were dissolved in 270 g of pure water, was prepared, and this solution was also added. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 2.0. The concentration of the slurry at this time was 21.1% by mass. This slurry was concentrated at 102°C for 7 hours such that the slurry concentration was 28.8% by mass.

[0043] The concentrated slurry was spray dried using a rotary-disc type spray dryer in that the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, and then these particles were finally calcined at 650°C for 3 hours.

Example 2

[0044] A fluid bed catalyst was prepared in a manner identical to that of Example 1, except that the composition of the prepared fluid bed catalyst was represented by $\text{Mo10 Bi0.5 Fe1.1 Ni4.0 Ce0.4 La0.2 Cr1.0 Co2.0 P0.2 B0.2 K0.2 Si35}$ and the prepared particles were calcined under conditions which are shown in Table 1-3. Moreover, nitrates of La and Co were used as a raw material of La and Co and they were added next to nickel nitrate.

40 Example 3

[0045] A fluid bed catalyst was prepared in a manner identical to that of Example 1, except that the composition of the prepared fluid bed catalyst was represented by $\text{Mo10 Bi0.5 Fe1.3 Ni5.0 Ce0.3 Cr0.6 Mg1.0 Zr0.2 K0.2 Si35}$ and the prepared particles were calcined under conditions which are shown in Table 1-3. Moreover, nitrates of Mg and Zr were used as a raw material of Mg and Zr and they were added next to nickel nitrate.

Example 4

[0046] A fluid bed catalyst was prepared in a manner identical to that of Example 1, except that the composition of the prepared fluid bed catalyst was represented by $\text{Mo10 Bi0.3 Fe1.1 Ni6.0 Ce0.2 Pr0.1 Cr0.8 Zn0.2 P0.3 K0.1 Rb0.1 Si40}$ and the prepared particles were calcined under conditions which are shown in Table 1-3. Moreover, nitrates of Pr, Zn and Rb were used as a raw material of Pr, Zn, and Rb and they were added next to nickel nitrate.

Example 5

[0047] A fluid bed catalyst was prepared in a manner identical to that of Example 1, except that the composition of the prepared fluid bed catalyst was represented by $\text{Mo10 Bi0.4 Fe0.9 N15.5 Ce0.4 Cr1.2 Mn0.4 W0.4 Pd0.01 P0.2 B0.2 K0.2 Si35}$ and the prepared particles were calcined under conditions which are shown in Table 1-3. Moreover,

nitrates of Mn and Pd were used as a raw material of Mn and Pd and they were added next to nickel nitrate. Ammonium paratungstate was used as a raw material of W and this was added next to ammonium paramolybdate.

Example 6

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[0048] A fluid bed catalyst the composition of which is represented by $Mo_{10} Bi_{0.4} Fe_{1.2} Ni_{6.0} (FeSb_{1.1})_3 Ce_{0.3} Cr_{0.8} P_{0.1} B_{0.1} K_{0.2} Si_{35}$, was produced by the following processes.

10

[0049] 348.9 g of ammonium paramolybdate was dissolved in 300 g of pure water. After that, 2.3 g of 85%-phosphoric acid and 0.4 g of boric anhydride were further added. A solution, in which 38.4 g of bismuth nitrate, 4.0 g of potassium nitrate, 344.9 g of nickel nitrate, 63.3 g of chromium nitrate, 25.7 g of cerium nitrate, and 25.0 g of citric acid were added to 270 g of 3.3%-nitric acid, was mixed with the prepared solution. After that, 2078.6 g of 20%-silica sol was also added. A solution, in which 95.8 g of iron nitrate and 25.0 g of citric acid were dissolved in 270 g of pure water, was prepared, and this solution was also added. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 2.3. The concentration of the slurry at this time was 21.1% by mass.

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This slurry was concentrated at 102°C for 7 hours such that the slurry concentration was 28.8% by mass. After that, 369.1 g of 40%-iron antimonate slurry was added.

[0050] The concentrated slurry was spray dried using a rotary-disc type spray dryer, and the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, these particles were finally calcined at 650°C for 3 hours.

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Example 7

[0051] A fluid bed catalyst of which the composition is identical to the composition of the fluid bed catalyst of Example 3 was produced by the following processes.

25

[0052] 409.8 g of ammonium paramolybdate was dissolved in 2,000 g of pure water. A solution, in which 56.3 g of bismuth nitrate, 4.7 g of potassium nitrate, 337.6 g of nickel nitrate, 55.7 g of chromium nitrate, 30.2 g of cerium nitrate, 59.5 g of magnesium nitrate, 12.4 g of zirconium nitrate, and 25.0 g of citric acid were added to 270 g of 3.3%-nitric acid, was mixed to the prepared solution. After that, 2441.0 g of 20%-silica sol was also added. A solution, in which 121.9 g of iron nitrate and 25.0 g of citric acid were dissolved in 270 g of pure water, was prepared, and this solution was also added. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 2. The concentration of the slurry at this time was 14.7% by mass. This slurry was concentrated at 102°C for 2 hours such that the slurry concentration was 21.1% by mass.

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[0053] The concentrated slurry was spray dried using a rotary-disc type spray dryer, and the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, these particles were finally calcined at 650°C for 3 hours.

Example 8

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[0054] A fluid bed catalyst of which the composition is identical to the composition of the fluid bed catalyst of Example 1 was produced by the following processes.

45

[0055] 409.4 g of ammonium paramolybdate was dissolved in 3,000 g of pure water. After that, 2.7 g of 85%-phosphoric acid and 0.5 g of boric anhydride were further added. A solution, in which 45.0 g of bismuth nitrate, 4.7 g of potassium nitrate, 404.7 g of nickel nitrate, 74.2 g of chromium nitrate, 30.2 g of cerium nitrate, and 25.0 g of citric acid were added to 270 g of 3.3%-nitric acid, was mixed to the prepared solution. After that, 2438.6 g of 20%-silica sol was also added. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 5.0. This slurry was heated at 99°C for 1.5 hours. A solution, in which 112.4 g of iron nitrate and 25.0 g of citric acid were dissolved in 270 g of pure water, was prepared, and this solution was also added. The concentration of the slurry at this time was 13.0% by mass and the pH thereof was 4.8. This slurry was concentrated at 102°C for 4 hours such that the slurry concentration was 22.4% by mass.

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[0056] The concentrated slurry was spray dried using a rotary-disc type spray dryer, and the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, these particles were finally calcined at 640°C for 3 hours.

Example 9

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[0057] A fluid bed catalyst of which the composition is represented by $Mo_{10} Bi_{0.6} Fe_{0.7} Ni_{7.0} (FeSb_{1.1})_4.5 Ce_{0.5} P_{0.2} B_{0.2} Te_{0.25} K_{0.6} Si_{40}$ was produced by the following processes.

[0058] 180.6 g of ammonium paramolybdate was dissolved in 1,200 g of pure water. After that, 3.9 g of 85%-phos-

phoric acid and 2049.1 g of 20%-silica sol were further added, in that order. A solution, in which 347.1 g of nickel nitrate, 37.0 g of cerium nitrate, 10.3 g of potassium nitrate, 25 g of citric acid, and 49.6 g of bismuth nitrate were added to 270 g of 3.3%-nitric acid, was mixed with the prepared solution. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 7.7. Then, the slurry was subjected to a heat treatment in which the slurry was refluxed at 99°C for 1.5 hours.

[0059] 5.4 g of metal tellurium, 4.5 g of ammonium paramolybdate, and 20 g of hydrogen peroxide were added to 250 g of water, and these were dissolved in water by stirring at 95-100°C. This prepared solution was cooled to room temperature and 25 g of citric acid and 48.2 g of iron nitrate were dissolved in the solution. While the prepared solution was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 9.2. 115.9 g of ammonium paramolybdate was added little by little and dissolved in the solution. After that, the pH of the solution was adjusted to 7 by adding aqueous ammonia.

[0060] This solution was mixed in the prepared slurry, and 480.8 g of 40%-iron antimonate slurry was further added. The concentration of the slurry at this time was 13.8% by mass and the pH thereof was 7.2. This slurry was concentrated at 102°C for 5.5 hours such that the slurry concentration was 17.2% by mass.

[0061] The concentrated slurry was spray dried using a rotary-disc type spray dryer, and the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, these particles were finally calcined at 580°C for 3 hours.

Example 10

[0062] A fluid bed catalyst of which the composition is identical to the composition of the fluid bed catalyst of Example 1 was produced by the following processes.

[0063] 409.4 g of ammonium paramolybdate was dissolved in 3,000 g of pure water. After that, 2.7 g of 85%-phosphoric acid and 0.5 g of boric anhydride were further added. A solution, in which 45.0 g of bismuth nitrate, 4.7 g of potassium nitrate, 404.7 g of nickel nitrate, 74.2 g of chromium nitrate, 30.2 g of cerium nitrate, and 25.0 g of citric acid were added to 270 g of 3.3%-nitric acid, was mixed with the prepared solution. After that, 2438.6 g of 20%-silica sol were further added. Another solution, in which 112.4 g of iron nitrate and 25.0 g of citric acid were dissolved in 270 g of pure water, was prepared, and this solution was also added. While the prepared slurry was stirred, 15%-aqueous ammonia was added to adjust the pH of the slurry to a pH of 3.0. This slurry was heated at 99°C for 1.5 hours. The concentration of the slurry at this time was 12.5% by mass. This slurry was concentrated at 102°C for 4 hours such that the slurry concentration was 22.1% by mass.

[0064] The concentrated slurry was spray dried using a rotary-disc type spray dryer, and the inlet temperature was 330°C and the outlet temperature was 160°C. After dried particles were heat treated at 250°C for 2 hours and 400°C for 2 hours, these particles were finally calcined at 650°C for 3 hours.

Comparative Example 1

[0065] A comparative fluid bed catalyst was prepared in a manner identical to that of Example 1, except that the concentration treatment for 7 hours was not carried out and the prepared particles were calcined under conditions which are shown in Table 1-4.

Comparative Example 2

[0066] A comparative fluid bed catalyst having a composition identical to that of Example 3 was prepared in a manner identical to that of Example 7, except heat treatment at 99°C for 2 hours was carried out instead of concentration treatment and the prepared particles were calcined under conditions which are shown in Table 1-4.

Comparative Example 3

[0067] A comparative fluid bed catalyst having a composition identical to that of Example 6 was prepared in a manner identical to that of Example 6, except that the concentration treatment for 7 hours was not carried out and the prepared particles were calcined under conditions which are shown in Table 1-4.

Comparative Example 4

[0068] A comparative fluid bed catalyst having a composition identical to that of Example 1 was prepared in a manner identical to that of Example 8, except that the solution containing iron nitrate and citric acid was added to the slurry after the concentration treatment and the prepared particles were calcined under conditions which are shown in Table

1-4.

[0069] The ammonoxidation of propylene was carried out under conditions explained above using the catalysts prepared in Examples and Comparative Examples.

[0070] The results are shown in Tables below.

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Table 1-1

| | Mo | Bi | Fe | Ni | FeSb Fe Sb | F | G | H | M | X | Y | SiO ₂ |
|----|----|-----|-----|-----|---------------|-------|-------|-----|------|-----|------|------------------|
| 1 | 10 | 0.4 | 1.2 | 6.0 | | Ce | Cr | | P | B | K | 35 |
| | | | | | 0.3 | | 0.8 | | 0.1 | 0.1 | 0.2 | |
| 2 | 10 | 0.5 | 1.1 | 4.0 | | Ce La | Cr Co | | P | B | K | 35 |
| | | | | | 0.4 | 0.2 | 1.0 | 2.0 | 0.2 | 0.2 | 0.2 | |
| 3 | 10 | 0.5 | 1.3 | 5.0 | | Ce | Cr Mg | Zr | | | K | 35 |
| | | | | | 0.3 | | 0.6 | 1.0 | 0.2 | | 0.2 | |
| 4 | 10 | 0.3 | 1.1 | 6.0 | | Ce Pr | Cr Zn | | P | | K | 40 |
| | | | | | 0.2 | 0.1 | 0.8 | 0.2 | | 0.3 | 0.1 | |
| 5 | 10 | 0.4 | 0.9 | 5.5 | | Ce | Cr Mn | W | Pd | P | K | 35 |
| | | | | | 0.4 | | 1.2 | 0.4 | 0.01 | 0.2 | 0.2 | |
| 6 | 10 | 0.4 | 1.2 | 6.0 | 3.0 | 3.3 | Ce | Cr | | P | B | K |
| | | | | | 0.3 | 0.3 | | 0.8 | | 0.1 | 0.1 | 35 |
| 7 | 10 | 0.5 | 1.3 | 5.0 | | Ce | Cr Mg | Zr | | | K | 35 |
| | | | | | 0.3 | | 0.6 | 1.0 | 0.2 | | 0.2 | |
| 8 | 10 | 0.4 | 1.2 | 6.0 | | Ce | Cr | | P | B | K | 35 |
| | | | | | 0.3 | | 0.8 | | 0.1 | 0.1 | 0.2 | |
| 9 | 10 | 0.6 | 0.7 | 7.0 | 4.5 | 5 | Ce | | P | B | Te | 40 |
| | | | | | 0.5 | 0.5 | | | 0.2 | 0.2 | 0.25 | |
| 10 | 10 | 0.4 | 1.2 | 6.0 | | Ce | Cr | | P | B | K | 35 |
| | | | | | 0.3 | 0.3 | 0.8 | | 0.1 | 0.1 | 0.2 | |

Example

Table 1-2

| | Mo | Bi | Fe | Ni | FeSb | F | G | H | M | X | Y | SiO ₂ |
|---------------------|----|-----|-----|-----|------|-----|----|-----|----|-----|-----|------------------|
| | Fe | Sb | Fe | Fe | Fe | Ge | Cr | | | P | B | K |
| 1 | 10 | 0.4 | 1.2 | 6.0 | | 0.3 | | 0.8 | | 0.1 | 0.1 | 0.2 |
| 2 | 10 | 0.5 | 1.3 | 5.0 | | 0.3 | Cr | Mg | Zr | | | 35 |
| 3 | 10 | 0.4 | 1.2 | 6.0 | 3.0 | 3.3 | Ge | Cr | | P | B | K |
| 4 | 10 | 0.4 | 1.2 | 6.0 | | | Ge | Cr | | 0.1 | 0.1 | 0.2 |
| | | | | | | | | | | P | B | K |
| | | | | | | | | | | 0.1 | 0.1 | 0.2 |
| | | | | | | | | | | | | 35 |
| Comparative Example | | | | | | | | | | | | |

Table 1-3

| | pH before concentration treatment | Concentration Treatment | | | Burning temperature [°C] | Contact time [sec.] | Yield of acrylonitrile [%] | | | Compressive strength $\times 10^{-3}$ [N/particle] |
|----------|-----------------------------------|--|---|--------------------------------------|--------------------------|---------------------|----------------------------|------|------|--|
| | | Concentration before concentration treatment [%] | Concentration after concentration treatment [%] | Concentration treatment time [hours] | | | Progress time [hour] | 50 | 500 | |
| 1 | 2.2 | 21.1 | 28.8 | 7.0 | 650 | 2.4 | 82.9 | 82.9 | 83.0 | 150 |
| 2 | 2.5 | 21.1 | 28.7 | 7.0 | 650 | 2.3 | 82.6 | 82.6 | 82.5 | 150 |
| 3 | 2.3 | 21.0 | 28.6 | 7.0 | 640 | 2.4 | 82.8 | 82.6 | 82.7 | 135 |
| 4 | 1.8 | 21.1 | 28.7 | 7.0 | 660 | 2.1 | 82.5 | 82.6 | 82.5 | 140 |
| 5 | 2.0 | 21.0 | 28.7 | 7.0 | 650 | 2.3 | 82.6 | 82.4 | 82.3 | 145 |
| 6 | 2.3 | 21.1 | 28.7 | 7.0 | 650 | 2.2 | 83.1 | 83.0 | 83.1 | 160 |
| 7 | 2.0 | 14.7 | 21.1 | 2.0 | 640 | 2.7 | 82.5 | 82.3 | 82.3 | 120 |
| 8 | 2.3 | 12.6 | 22.0 | 4.0 | 640 | 2.3 | 82.8 | 82.6 | 82.6 | 155 |
| 9 | 7.2 | 13.8 | 17.2 | 5.5 | 580 | 2.3 | 83.1 | 82.9 | 82.7 | 195 |
| 10 | 3.0 | 12.5 | 22.1 | 4.0 | 650 | 2.4 | 82.7 | 82.6 | 82.6 | 145 |
| Examples | | | | | | | | | | |

Table 1-4

| pH before concentration treatment | Concentration before concentration treatment [%] | Concentration after concentration treatment [%] | Concentration treatment time [hours] | Burning temperature [°C] | Contact time [sec.] | Yield of acrylonitrile [%] | | Compressive strength $\times 10^{-3}$ [N/particle] |
|--|--|---|---|--------------------------------|---------------------------|----------------------------|------|---|
| | | | | | | Progress time [hour] | 50 | |
| Comparative Examples | | | | | | | | |
| 1 | - | 21.1 | 21.1 | 0.0 | 630 | 3.3 | 81.6 | 81.4 |
| 2 | - | 14.7 | 14.7 | heating 2.0 | 640 | 3.1 | 81.5 | 81.3 |
| 3 | - | 21.1 | 21.1 | 0.0 | 630 | 2.5 | 82.0 | 81.7 |
| 4 | 4.8 | 13.0 | 22.4 | 4.0 | 640 | 2.4 | 81.8 | 81.8 |
| | | | | | | | | 90 |

INDUSTRIAL APPLICABILITY

[0071] The production method of the present invention can yield a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst with an excellent reproducibility. The molybdenum-bismuth-iron containing composite oxide fluid bed catalyst produced by the present invention has a high activity and this yields the target ammonoxidation product at high yield. For example, by using the molybdenum-bismuth-iron containing composite oxide fluid bed catalyst produced by the present invention in an ammonoxidation of propylene, acrylonitrile can be obtained at high yield.

10 Claims

1. A method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst which is a method for producing a composite oxide catalyst containing components (1) molybdenum, (2) bismuth, (3) iron, (4) nickel, (5) at least one element selected from lithium, sodium, potassium, rubidium, cesium and thallium, and (6) silica, as essential components, wherein a slurry containing at least components (1), (2), (3), and (6) is concentrated in a range of 50-120°C, so that the concentration difference of the slurry between before and after the concentration treatment is in a range of 2-15% by mass.
2. A method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst according to claim 1, wherein the concentration of the slurry after the concentration treatment is in a range of 15-35% by mass.
3. A method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst according to claim 1 or 2, wherein the pH of the slurry before the concentration treatment is adjusted in a range of 1-4.
4. A method for producing a molybdenum-bismuth-iron containing composite oxide fluid bed catalyst according to one of claims 1 to 3, wherein the composite oxide fluid bed catalyst has a composition represented by



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in the formula, Mo, Bi, Fe, Ni, and (FeSbd) denote molybdenum, bismuth, iron, nickel and iron antimonate; F denotes at least one element selected from yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, aluminum, and gallium; G denotes at least one element selected from magnesium, calcium, strontium, barium, chromium, manganese, cobalt, copper, zinc, and cadmium; H denotes at least one element selected from titanium, zirconium, vanadium, niobium, tantalum, tungsten, germanium, tin, lead, and antimony; M denotes at least one element selected from ruthenium, rhodium, palladium, rhenium, osmium, iridium, platinum, and silver; X denotes at least one element selected from boron, phosphorus, and tellurium; Y denotes at least one element selected from lithium, sodium, potassium, rubidium, cesium, and thallium; O denotes oxygen; SiO_2 denotes silica; symbols a, b, c, d, e, f, g, h, m, x, y, i, and j denote atomic ratio; when the atomic ratio of Mo is 10, a is in a range of 0.2-1.5, b is in a range of 0.7-15, c is in a range of 3-12, d is in a range of 0.8-2, e is in a range of 0-20, f is in a range of 0.1-1.5, g is in a range of 0-5, h is in a range of 0-3, m is in a range of 0-1.0, x is in a range of 0-3, y is in a range of 0.05-1.5, i is the number of oxygen elements in metal oxides, which are formed by combining these elements; and j is in a range of 20-200.

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INTERNATIONAL SEARCH REPORT

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| International application No. |
| PCT/JP02/03446 |

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| A. CLASSIFICATION OF SUBJECT MATTER |
| Int.Cl ⁷ B01J23/88, C07C253/26, 255/08 |

According to International Patent Classification (IPC) or to both national classification and IPC

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| B. FIELDS SEARCHED |
|--------------------|

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl⁷ B01J21/00-37/36

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2002
Kokai Jitsuyo Shinan Koho 1971-2002 Jitsuyo Shinan Toroku Koho 1996-2002

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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| C. DOCUMENTS CONSIDERED TO BE RELEVANT |
|--|

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|--|-----------------------|
| E, X | JP 2001-187772 A (Mitsubishi Rayon Co., Ltd.), 10 July, 2001 (10.07.01), Claim 1; example 1 (Family: none) | 1-4 |
| X A | JP 63-250357 A (Nitto Chemical Industry Co., Ltd.), 18 October, 1988 (18.10.88), Claims; page 4, lower left column, lines 3 to 8; example 1 (Family: none) | 1-3 4 |
| X A | EP 340909 A1 (Nitto Chemical Industry Co., Ltd.), 08 November, 1989 (08.11.89), Claims; examples & US 5158787 A & JP 1-257125 A | 1-2 3-4 |

Further documents are listed in the continuation of Box C. See patent family annex.

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| Date of the actual completion of the international search 02 July, 2002 (02.07.02) | Date of mailing of the international search report 16 July, 2002 (16.07.02) |
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